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TITLE: Thermoelectric element has several pn-junctions along articulation direction and integrated insulating material between n-type and p-type semiconductor materials

PRIORITY-DATA: 2000JP-0028211 (February 4, 2000)

PATENT-FAMILY:

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INT-CL (IPC): H01L035/32, H01L035/34

ABSTRACTED-PUB-NO: JP2001217469A

BASIC-ABSTRACT:

NOVELTY - The thermoelectric element which has several pn-junctions along the articulation direction, has an insulating material such as silicon group and ceramic powder integrated and provided between a n-type semiconductor material (2) and a p-type semiconductor material (1).

DETAILED DESCRIPTION - An INDEPENDENT CLAIM is also included for thermoelectric

element manufacturing method.

USE - Thermoelectric element.

ADVANTAGE - Since loss of pn-junctions is reduced greatly, thermoelectric conversion efficiency is improved, thus weight reduction is achieved and manufacturing cost is reduced.

DESCRIPTION OF DRAWING(S) - The figure shows an explanatory drawing explaining the manufacturing method of thermoelectric element.

p-type semiconductor material 1

n-type semiconductor material 2

PAT-NO: JP02001217469A

DOCUMENT-IDENTIFIER: JP 2001217469 A

TITLE: THERMOELECTRIC CONVERSION ELEMENT AND ITS MANUFACTURING METHOD

PUBN-DATE: August 10, 2001

INVENTOR-INFORMATION:

| NAME | COUNTRY |
|---|---|
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INT-CL (IPC): H01L035/32, H01L035/34

ABSTRACT:

PROBLEM TO BE SOLVED: To provide a thermoelectric conversion element that is in a configuration where the thermoelectric conversion efficiency of an Si-group material that is an inexpensive and light thermoelectric conversion material has been improved extremely and at the same time uses and Si group that is in a configuration for facilitating manufacturing, and its manufacturing method.

SOLUTION: When the thermoelectric conversion element is subjected to compression molding in p/n/p/n/p/ configuration for integration sintering by alternately arranging n-type and p-type material power and including an insulation material such as Si-system and ceramic power outside the scheduled part of pn junction, integration can be facilitated extremely, and at the same time loss due to electrode junction can be reduced to almost zero. At the same time, joining is made to a pn junction that is located at high-temperature and low- temperature sides for forming an element via a hetero metal when a temperature gradient is given to the thermoelectric conversion element, thus improving electromotive force and the amount of electricity.

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| (51)Int.Cl.⁷ | 識別記号 | F I | テーマコード*(参考) |
|---|---|---|---|
| H01L 35/32 | | H01L 35/32 | A |
| 35/34 | | 35/34 | |

審査請求　未請求　請求項の数8　OL　（全 9 頁）

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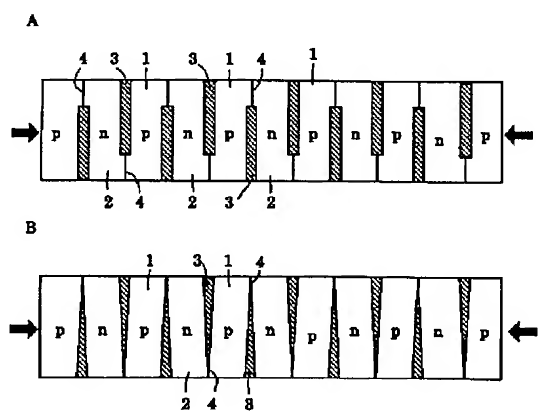
(54)【発明の名称】　熱電変換素子とその製造方法

(57)【要約】
【課題】　安価で軽量な熱電変換材料であるSi基材料の熱電変換効率を著しく高めた構成であるとともに、製造が容易な構成からなるSi基の熱電変換材料を用いた熱電変換素子とその製造方法の提供。
【解決手段】　n型とp型の材料粉末を交互に配置し、Si系やセラミックスの粉末など絶縁材を、pn接合予定部以外に介在させることにより、p/n/p/n/p/と圧縮成形して一体化焼結すると、一体化が極めて容易になると共に、電極接合によるロスはほとんど無視できるほど小さくなり、かつ熱電変換素子に温度勾配を与えた際の高温側と低温側に位置するpn接合部に異種金属を介して接合し、素子化することにより、起電力および電力量が向上する。



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【特許請求の範囲】

【請求項1】 n型半導体材料とp型半導体材料間に、絶縁材料を介在して一体化され、連接方向に単数又は複数のpn接合部を有する熱電変換素子。

【請求項2】 n型半導体材料とp型半導体材料間に、電極材料と絶縁材料を介在して一体化され、連接方向に単数又は複数のpn接合部を有する熱電変換素子。

【請求項3】 一体化が、粉末冶金法、圧着法、焼成法又は溶接によるものである請求項1又は請求項2に記載の熱電変換素子。

【請求項4】 電極材料が温度勾配を与えられた際の高温側と低温側で異なる材料である請求項3に記載の熱電変換素子。

【請求項5】 n型半導体粉末材料とp型半導体粉末材料を、板状又は粉末の絶縁材料あるいはさらに板状又は粉末の電極材料を介して配置し、粉末冶金法により一体化し、得られた一体型の熱電変換素子内に単数又は複数のpn接合部を形成する熱電変換素子の製造方法。

【請求項6】 バルクのn型半導体材料とp型半導体材料を、板状又はペースト状の絶縁材料あるいはさらに板状又はペースト状の電極材料を介して配置し、圧着法により一体化し、得られた一体型の熱電変換素子内に単数又は複数のpn接合部を形成する熱電変換素子の製造方法。

【請求項7】 バルクのn型半導体材料とp型半導体材料を、ペースト状の絶縁材料あるいはさらにペースト状の電極材料を介して配置し、焼成法により一体化し、得られた一体型の熱電変換素子内に単数又は複数のpn接合部を形成する熱電変換素子の製造方法。

【請求項8】 素子として温度勾配を与えた際の高温側と低温側にそれぞれ異なる電極材料を配置する請求項5から請求項7のいずれかに記載の熱電変換素子の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】この発明は、Si基の熱電変換材料などを用いた製造容易な熱電変換素子に係り、n型およびp型半導体を交互に並べて各々に電極材料と絶縁材料を介在させて一体化成形にてpn接合し、Si基材料の熱電変換効率を著しく高めて高効率に電気エネルギーを取り出すことが可能な熱電変換素子とその製造方法に関する。

【0002】

【従来の技術】熱電変換素子は、近年の$CO_2$削減をはじめとするエネルギー、環境問題の点から注目を浴びており、特に熱エネルギーの有効利用の観点から実用化が期待されているデバイスである。

【0003】例えば、焼却炉や発電所のタービンなどの廃熱を利用して電気エネルギーに変換するシステムや、屋外や宇宙で簡単に電気を得るための携帯発電装置、ガス機器の炎センサー、太陽電池や燃料電池との併用、自動車

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の内燃機関の廃熱を利用し、燃費向上させる等、非常に広範囲の用途が検討されている。

【0004】しかし、今までに知られている熱電変換素子は、一般に変換効率が低い、使用温度範囲が非常に狭い、使用元素の環境汚染の問題がある、原料および製造コストが高い等の理由から汎用されるには至っていない。

【0005】この熱エネルギーから電気エネルギーへの変換効率は、性能指数ZTの関数であり、ZTが高いほど高くなる。この性能指数ZTは、$ZT=S^2\sigma T/\kappa$ 式のように表されている。ここで、Sは熱電材料のゼーベック係数、$\sigma$は電気伝導率、$\kappa$は熱伝導率、そしてTは熱電素子の高温側($T_H$)と低温側($T_L$)の平均値で表した絶対温度である。

【0006】現在、最も高い性能指数の熱電材料はスクッテルダイト型結晶構造を有する$IrSb_3$(T.Caillet, A.Borshchrysky and J.-P. Fleurial : Proc. 12th Int. Conf. on Thermoelectrics, (Yokohama, Japan, 1993)P132.)であり、そのZT値は約2.0を示す。しかしながら、Irの原料コストが高いために、実用化には至っていない。

【0007】また、低温で高い性能指数を示す$Bi_2Te_3$はペルチェ素子として半導体等の冷却用素子として使用されているが、融点が530Kと低いため、使用温度範囲が狭いという問題があった。

【0008】一方、コストと環境の点からは、Fe-Si系材料が有望であるとされているが、この系は性能指数(ZT)は0.2以下であり、熱電変換材料として要求される特性には迄かに満たないものであった。

【0009】Si-Ge系材料は、B.Abeles (Phys. Rev. 131, 1906, (1963))がSi-Ge合金の熱伝導率の組成依存性を調査し、SiとGeを合金化することにより熱伝導率が大きく低下できることを報告した。彼らの報告ではGeの含有量が20～30原子%含有しなければ熱伝導の低下は見られないと報告された。

【0010】しかし、Geの原料コストが高いこと、また、SiとGeは全律固溶の液相線と固相線の幅広い状態をもち、溶解やZone Leveling法では組成を均一に作製するのが困難という問題あった。また、組成を均一にするためにホットプレスによる方法も試みられているが、量産性に乏しいものであった。

【0011】さらに、特開平11-54808号公報には、Si-Ge合金粉末を用いて、円板状のn型およびp型の予備成形体を作製し、n,p,n,pの順に4枚予備成形体を積層して焼結し、その後これを直方体に加工し、さらにn,p間に分離部を形成する切削加工を行い、折り畳むがごとくの形状を有した熱電変換素子を作製する方法が提案されている。しかし、製造工程が煩雑で加工に手間を要するだけでなく、材料自体の特性も劣るものである。

【0012】

【発明が解決しようとする課題】発明者らは、半導体デ

バイスとして広く使用されているSiが極めて高いゼーベック係数を有することに着目して、特にSi基の材料の熱電特性を評価した結果、Siに0.001～20原子%という少量の元素の添加で高い性能指数を有する熱電変換材料となり得ることを知見した(WO99/22410)。

【0013】Siは、環境負荷も小さく資源も豊富にあり、原料コストも比較的安い上、軽いという特徴がある。さらに、発明者らは、接合部の電極を選定することによりゼーベック係数を大きくすることができ、取り出せる電力として向上することを見い出した。

【0014】しかしながら、熱電変換材料を素子として使用する際に、p型、n型の材料の接合部及び電極に関する接合が良好でない場合、取り出せる電力にロスが生ずる。これは電極材質を選定した場合でも起こり得る。さらに高温端の電極の接合は熱電材料と電極材質の原子の拡散や場合によっては合金化されたり、電極材質との間の熱膨張係数の差が大きい場合は電極の剥がれやクラックの原因となる問題があった。

【0015】この発明は、熱電変換材料、特に安価で軽量なSi基材料の熱電変換効率を著しく高めた構成であるとともに、製造が容易な構成からなるSi基の熱電変換材料を用いた熱電変換素子とその製造方法の提供を目的としている。

【0016】

【課題を解決するための手段】発明者らは、Si基熱電変換材料などの熱電特性を損なうことなく、熱電変換素子として電力を取り出せる方法として、n型とp型の材料を一体化して作製することに着目し、一体化方法として、粉末をホットプレス、放電プラズマ焼結、熱間静水圧プレスなどの熱間圧縮成形、または冷間圧縮成形後に焼結するなどの粉末冶金手段の他、Si基板上に粉末材料のレジストをパターニングして積層させる方法で試みた。

【0017】発明者らは、一体化に際して、Si系やセラミックスの粉末などの絶縁材を、pn接合予定部以外に介在させることにより、一体化が極めて容易になると共に、pn接合部のロスは大幅に低下し、熱電変換効率が向上すること、さらに材料を交互に配置してp/n/p/n/p/と一体化した焼結体を作製することにより、電極接合によるロスはほとんど無視できるほど小さくなり、又熱応力により接合部が剥がれたり割れたりすることのない素子を作製できることを知見した。

【0018】また発明者らは、熱電変換素子に温度勾配を与えた際の高温側と低温側に位置するpn接合部に異種金属を介して接合し、素子化することを試み、接合方法として粉末焼結時にp/nの粉末の境面に金属粉末を挿入する方法と、p/n境面に金属板を介する方法で行い、前記粉末冶金手段にて接合し、一体化された素子の電圧及び電流を測定した結果、金属材質を最適に選ぶことにより起電力および電力量が向上することを知見し、この発明を完成した。

【0019】さらに、粉末冶金での接合だけでなく、Si基材料の焼結材、溶製材のバルクと電極材料を、抵抗加熱、通電焼結、熱間加圧などの圧着法、ペースト材料を用いた焼成法、さらには溶接法などにより接合することが可能であり、最適な電極材質を選択することにより、電極接合のロスはなく、また起電力及び電力量が向上することを知見した。

【0020】この発明は、n型半導体材料とp型半導体材料間に、絶縁材料を介在させるか、電極材料と絶縁材料を介在させて一体化された単数又は複数のpn接合部を有することを特徴とする熱電変換素子である。

【0021】また、この発明は、n型半導体粉末材料とp型半導体粉末材料を、板状又は粉末の絶縁材料あるいはさらに電極材料を介して配置し、粉末冶金法により一体化するか、あるいは、固体のn型半導体材料とp型半導体材料を、板状、粉末又はペースト状の絶縁材料あるいはさらに電極材料を介して配置し、冷間又は熱間の圧着法あるいは焼成法により一体化し、得られた一体型の熱電変換素子内に単数又は複数のpn接合部を形成することを特徴とする熱電変換素子の製造方法である。

【0022】さらに、この発明は、素子として温度勾配を与えた際の高温側と低温側にそれぞれ異なる電極材料を配置することを特徴とする熱電変換素子とその製造方法である。

【0023】

【発明の実施の形態】この発明による熱電変換素子の製造方法を図面に基づいて詳述する。図1Aは、粉末冶金法にて直接pn接合する場合であり、p型半導体材料粉末1とn型半導体材料粉末2及び絶縁材料粉末3としてそれぞれ焼結可能な材料粉末を用いる。

【0024】例えば箱状の金型内に、音叉型の仕切り部材を開き側が交互に入れ代わるように用いて、p型半導体材料粉末1とn型半導体材料粉末2及び絶縁材料粉末3を交互に挿入し、仕切り部材を取り除いて、上面に蓋を設けて金型中心へ矢印方向に圧縮して成形体となす。

【0025】成形体は、p型半導体材料粉末1とn型半導体材料粉末2がpn接合予定部4を除いて絶縁材料粉末3にて隔てられて交互に配列した構成からなる。ここで、この成形体を焼結することで、各半導体材料間は絶縁材料が一体化され、焼結にて直接接合されたpn接合部を各半導体材料の連接方向に複数箇有する、一体型の熱電変換素子が得られる。

【0026】また、図1Aにおいて、絶縁材料粉末3部分を、予め成形した絶縁材板、絶縁材シートなどに変えても、焼結による直接pn接合部が複数箇所の連接型の熱電変換素子を製造できることは、もちろんのこと、直接pn接合部が一か所の1ペア型の熱電変換素子も同様に製造できる。

【0027】図1Bに示す製造例は、箱状の金型内に、三角形の仕切り部材を開き側が交互に入れ代わるように用い、

かつ三角形の仕切り部材の所要先端部には絶縁材料粉末が入らないようにして、p型半導体材料粉末1とn型半導体材料粉末2及び絶縁材料粉末3を交互に挿入し、仕切り部材を取り除いて、金型中心へ矢印方向に圧縮して成形体となす。

【0028】成形体は、p型半導体材料粉末1とn型半導体材料粉末2がpn接合予定部4を除いて絶縁材料粉末3にて隔てられて交互に配列した構成となる。この成形体を焼結することで、各半導体材料間は絶縁材料が一体化され、焼結にて直接接合されたpn接合部を各半導体材料の連接方向に複数箇有する、一体型の熱電変換素子が得られる。

【0029】図2Aに示す製造例は、箱状の金型内に、図示のごとく、p型半導体材料粉末1とn型半導体材料粉末2との間に、絶縁材料粉末3、電極材料粉末5,6を装填し、絶縁材料粉末3と電極材料粉末5,6の挿入位置が交互に入れかわるように装填し、金型中心へ矢印方向に圧縮して図2Bに示すごとく成形体となす。

【0030】また、図で完成した熱電変換素子の下部を熱源に近接させた高温側、上部を低温側とした温度勾配を与えた場合、電極材料粉末には、高温側6と低温側5でそれぞれ異なる材質の金属、合金粉末を用いる。

【0031】この成形体を焼結することで、各半導体材料間は絶縁材料が一体化され、焼結にて電極材料を介して接合されたpn接合部を各半導体材料の連接方向に複数箇有する、一体型の熱電変換素子が得られる。

【0032】また、絶縁材料粉末3、電極材料粉末5,6を図2Aに示す矩形形状に装填する他、図2Cに示すごとく、p型半導体材料粉末1とn型半導体材料粉末2間に三角形状に装填することも可能であり、絶縁材料の量や絶縁寸法などに応じて任意の形態を採用し得る。

【0033】図3Aに示す製造例は、前述の図1Bと同様であるが、図1Bの絶縁材料粉末を配置しない三角頂点部のpn接合予定部に、薄板状の電極材料7,8を配置して他は絶縁材料粉末3を装填したもので、圧縮成形体となした後に焼結することで、各半導体材料間は絶縁材料が一体化され、電極材料7,8を介して焼結にて接合されたpn接合部を各半導体材料の連接方向に複数箇所有する、一体型の熱電変換素子が得られる。ここでも電極材料7,8には、図で完成した熱電変換素子の下部を熱源に近接させた高温側、上部を低温側とした温度勾配を与えた場合、電極材料には、高温側8と低温側7でそれぞれ異なる材質の金属、合金を用いている。

【0034】図3Bに示す製造例は、溶解合金からブロック状に固化した溶製材あるいはブロック状に圧縮成形して焼結した焼結材などのp型半導体材料10とn型半導体材料11間に、板材に加工した絶縁材料12、電極材料13,14を配置して、これらを当接させ、熱間又は冷間での圧着手段にて一体化することにより、各半導体材料間は絶縁材料が一体化され、その連接方向に電極材料を介して接合された複数のpn接合部が配置された一体型の熱電変換素子が得られる。

【0035】図3Cに示す製造例は、前記の溶製材あるいは焼結材などのp型半導体材料10とn型半導体材料11の片面に、ペースト状絶縁材料15、ペースト状電極材料16,17を塗布して、これらを当接させ、焼成にて一体化することにより、各半導体材料間は絶縁材料が一体化され、その連接方向に電極材料を介して接合された複数のpn接合部が配置された一体型の熱電変換素子が得られる。

【0036】ここでも電極材料16,17には、図で完成した熱電変換素子の下部を熱源に近接させた高温側、上部を低温側とした温度勾配を与えた場合、電極材料には、高温側17と低温側16でそれぞれ異なる材質の金属、合金を用いている。また、上記のペースト状の絶縁材料15、電極材料16,17に変えて、焼結用の絶縁材料粉末、電極材料粉末を用いて、通電焼結などの手段で一体化することも可能である。

【0037】一体化する半導体材料を配置する方法としては、p型から始まりn型で終わる偶数型の他、図1に示すごとく、p,n,pやn,p,n,p,nなどの奇数型でもよく、いずれにしても連接部に1以上のpn接合部を有する構成とする必要がある。

【0038】一体化成形方法には、粉末冶金法、圧着法、焼成法、溶接法などが採用できる。粉末冶金法は、例えばSi-Geのn型半導体粉末材料、p型半導体粉末材料並びに金属材料の板又は粉末を、例えば図1の熱電変換素子と略相似形の金型などに個別又は同時に入れて、粉末をホットプレス、放電プラズマ焼結、熱間静水圧プレスなどの熱間圧縮成形又は冷間圧縮成形後に焼結するなどの粉末冶金手段にて一体化することができる。

【0039】また、Si基材料、Si-Ge合金の焼結材、溶製材と電極材料を、抵抗加熱、通電焼結、熱間加圧などの圧着法、ペースト材料を用いた焼成法、さらには溶接法などにより、pn接合することが可能である。上記の一体化成形方法は、半導体材料、電極用材料、絶縁材料の種類や形態に応じて、最適な方法を選択するとよい。

【0040】さらに、上述の粉末冶金法の他、Si基板、$Si_{1-x}Ge_x$($x<0.20$)基板上に粉末材料のレジストをパターニングして積層させる方法が採用できる。具体的には、Si、Geを電子ビーム加熱して蒸発させるPVD法、$SiH_4$、$GeH_4$からSi、Geを積層させるCVD法などがあり、マスクを介してpn接合並びに金属層の接合も可能である。積層後、400～800℃で熱処理することにより、積層膜が結晶化し特性が向上する。

【0041】絶縁材料としては、電気的絶縁が可能な公知のいずれの材料も採用できる。比抵抗値は$10^2\ \Omega\cdot m$以上が好ましい。半導体材料と焼結、圧着、接着が可能で、熱膨張係数が近似している材料が好ましい。また絶縁材料から熱が伝導すると熱電変換材料の温度勾配が小さくなるため、熱伝導率の小さな材料が好ましい。例えば、半

導体材料がSi基材料、Si－Ge合金の場合、Si、ノンドープSi－Ge、$SiO_2$、$Si_3N_4$、BN、SiC、$Al_2O_3$、TiN、各種フェライトなどを用いることができる。

【0042】電極材料としては、金属、樹脂などのいずれの材質も使用でき、比較的耐食性に優れ、しかも熱電変換材料に着設しやすい金属、合金が好ましい。特に高温で高特性を示す熱電材料では高融点の金属、合金を使用することが好ましい。例えば、熱電変換材料の高温側の材料としては、Zr,Au,Ag,Pt,Cu,Ti,Mo,Zn,W,C、低温側の材料としてはBi,Sn,Ag,Cu,Pt,Al,Au,Fe,Mo,Zn,Pbが好ましい。又、これらの金属の合金、あるいはこれらの金属を含む合金を用いることもできる。

【0043】熱電変換材料の高温側と低温側に使用する金属材料の種類、組合せは、熱電変換材料種によってそれぞれ異なる。例えば、$FeSi_2$化合物の場合は、高温側にPt、低温側にCu、$Bi_2Te_3$化合物の場合は、高温側にPt、低温側にAl、$Si_{1-x}Ge_x$($x<0.20$)の場合は、高温側にPt、低温側にAl、などが好ましい。

【0044】この発明において、熱電変換材料には、公知のいずれの材質も採用可能である。特にSi基材料、$Si_{1-x}Ge_x$($x<0.20$)の組成からなる熱電変換材料の他、$Bi_2Te_3$系材料が好ましい。

【0045】Si基材料は、組成が$Si_{1-x}A_x$($x<0.20$)で、Aには4族元素(Ge,C,Sn)、3-5族化合物半導体、2－6族化合物半導体の少なくとも1種を添加し、後述するドーパント元素によってキャリアー濃度を$10^{17}$～$10^{21}$($M/m^3$)に制御するもので、基本的に多結晶Siで各結晶粒内はほとんどがSiであり、粒界部に前記添加元素とドーパント元素、Si-Geの場合はGeとドーパント元素が同時に偏析した構造を特徴とする。

【0046】Si基材料は、Si半導体中のキャリアー濃度が$10^{17}$～$10^{21}$($M/m^3$)になるようにP,B,Alなど種々の添加元素の単独又は複合添加とその添加量を調整することにより、ゼーベック係数が極めて大きく、熱電変換効率を著しく高めることができ、生産性が良く品質が安定した安価な熱電変換材料である。

【0047】この発明のSi基材料において、特にSi-Geの場合は、Geが0.05原子%未満では熱伝導率が大きいため、高い性能指数は得られず、また、20原子%以上では熱伝導率は若干低下するが、同時に粒内のSiリッチ相にもGeが拡散し、固溶するため、Siの高いゼーベック係数が低下し、性能指数を低下させる原因となる。よって、Geの好ましい含有量は0.05以上、20原子%未満の範囲とする。特に好ましくは、3～10原子%である。

【0048】この発明において、SiをP型半導体またはN型半導体となすためのドーパント元素は、所要範囲内のキャリアー濃度で熱伝導率、電気抵抗を低下させると同時に、高いゼーベック係数を得るために添加するものである。熱電変換材料の用途を考慮すると、熱源、使用箇所や形態、扱う電流、電圧の大小などの用途に応じて、ゼーベック係数、電気伝導率、熱伝導率のいずれの特性に重点を置くかで変わるため、用途などに応じて選択元素とその添加量を選択することができる。添加量としては、0.001原子%～20原子%が好ましい。

【0049】p型半導体となすためのドーパント元素としては、pグループ群(Be,Mg,Ca,Sr,Ba,Zn,Cd,Hg,B,Al,Ga,In,Tl)、遷移金属元素$M_1$群($M_1$;Y,Mo,Zr)の各群から選択する1種又は2種以上が望ましい。中でも特に好ましい元素はB,Ga,Alである。

【0050】n型半導体となすためのドーパント元素は、nグループ群(N,P,As,Sb,Bi,O,S,Se,Te)、遷移金属元素$M_2$群($M_2$;Ti,V,Cr,Mn,Fe,Co,Ni,Cu,Nb,Ru,Rh,Pd,Ag,Hf,Ta,W,Re,Os,Ir,Pt,Au、但しFeは10原子%以下)、希土類元素群RE(RE;La,Ce,Pr,Nd,Pm,Sm,Eu,Gd,Tb,Dy,Ho,Er,Yb,Lu)の各群から選択する1種又は2種以上が望ましい。中でも特に好ましい元素はP,Cu,Asである。

【0051】

【実施例】実施例1

原料として、p型に$Si_{0.95}Ge_{0.05}$(B0.3at%)、n型に$Si_{0.95}Ge_{0.05}$(P0.4at%)を配合し、高周波真空溶解炉にて溶解したp型及びn型の熱電変換材料のインゴットを振動ミル及び窒素ガス中でジェットミルにて平均粒径約4μmに粉砕した。

【0052】得られた各粉末を図1Aの如くカーボン型にp型半導体材料粉末1とn型半導体材料粉末2がpn接合予定部4を除いて絶縁材料粉末3にて隔てられて交互に配列した構成となるように装填し1500～1600K×1h、圧力25～100MPaの条件でホットプレスにて一体化したpn接合部が10ヶ所ある熱電変換素子を作製した。

【0053】素子全体の寸法は5mm×75mm×15mmであった。その素子の一番両端に電極とリード線を接合し、一方を873Kの高温に加熱し、他方を373Kの温度勾配をつけ、それぞれの発生起電力と発生起電流および抵抗値をデジタルマルチメーターで測定し、得られた出力電力量を求めた。その結果を表1に示す。なお、電力比率は、以下の比較例1(絶縁材料なし)の出力電力を1として比較した。

【0054】比較例として、絶縁材料を挟まない場合の測定値(比較例1)およびPtペーストを介して接合した場合の測定値(比較例2)を同様に表1に示す。

【0055】実施例2

原料として、p型に$Si_{0.95}Ge_{0.05}$(B0.3at%)、n型に$Si_{0.95}Ge_{0.05}$(P0.4at%)を配合し、アーク溶解にて溶解したp型及びn型の熱電変換材料のインゴットをスタンプミル及びボールミルにて平均粒径約2μmに粉砕した。ボールミルはキシレン溶媒中で行った。

【0056】得られた各粉末を図2Aの如くp型半導体材料粉末1とn型半導体材料粉末2との間に、絶縁材料粉末3、粒径10μmの電極材料粉末5,6を装填し、絶縁材料粉末3と電極材料粉末5,6の挿入位置が交互に入れかわるように装填し、1100～1573K×600sec、圧力50MPaの条件で放電

プラズマ焼結し、pn接合部が10ヶ所ある熱電変換素子を作製した。

【0057】素子全体の寸法は5mm×75mm×15mmであった。その素子のその一番両端に電極とリード線を接合し、一方を873Kの高温に加熱し、他方を373Kの温度勾配をつけ、それぞれの発生起電力と発生起電流および抵抗値をデジタルマルチメーターで測定し、得られた出力電力量を求めた。その結果を表2に示す。なお、電力比率は、以下の比較例4(絶縁材料なし)の出力電力を1として比較した。

【0058】なお比較例として、絶縁材料を挟まない場合の測定値(比較例4)およびPtペーストを介して接合した場合の測定値(比較例5)、pn接合部に絶縁材を挟むが金属板を介さない素子の測定値(比較例3)を同様に表2に示す。

【0059】実施例3

原料として、p型に$Si_{0.95}Ge_{0.05}$(B0.3at%)、n型に$Si_{0.95}Ge_{0.05}$(P0.4at%)を配合し、高周波真空溶解炉にて溶解したp型及びn型の熱電変換材料のインゴットを振動ミル及び窒素ガス中でジェットミルにて平均粒径約4μmに粉砕した。得られたそれぞれの粉末を5mm×5mm×15mmのカーボン型に挿入し、1573K×1h、圧力50MPaでホットプレスした。

【0060】得られら焼結体には図3Cに示すようにp型の材料にはペースト状絶縁材料15と低温側電極ペースト16を、n型の材料にはペースト状絶縁材料15と高温側電極ペースト17を塗布し、その後1173K×30min、真空中で焼成し、pn接合部が10ヶ所ある熱電変換素子を作製した。

【0061】熱電変換素子の一番両端に電極とリード線を接合し、一方を873Kの高温に加熱し、他方を373Kの温度勾配をつけ、それぞれの発生起電力と発生起電流および抵抗値をデジタルマルチメーターで測定し、得られた出力電力量を求めた。その結果を表3に示す。なお、電力比率は、以下の比較例7(絶縁ペーストなし)の出力電力を1として比較した。

【0062】なお比較例として、絶縁ペーストを挟まない場合の測定値(比較例7)およびpn接合部に絶縁ペーストを挟むが電極ペーストを介さない素子の測定値(比較例6)を同様に表3に記す。

【0063】

【表1】

| No. | N型材料 | P型材料 | 絶縁材料 | 焼結条件 温度(K) | 焼結条件 圧力(Mpa) | 焼結条件 時間(h) | 起電力 (V) | 抵抗 (Ω) | 出力電力 (W) | 電力比率 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $Si_{0.95}Ge_{0.05}$ (P 0.4at%) | $Si_{0.95}Ge_{0.05}$ (B 0.3at%) | $Si_{0.95}Ge_{0.05}$ | 1523 | 50 | 1 | 3.05 | 2.48 | 3.75 | 1.04 |
| 2 | 〃 | 〃 | $Si_{0.95}Ge_{0.05}$ | 1573 | 50 | 1 | 3.13 | 2.44 | 4.02 | 1.12 |
| 3 | 〃 | 〃 | $SiO_2$ | 1573 | 30 | 1 | 3.12 | 2.46 | 3.96 | 1.10 |
| 4 | 〃 | 〃 | $SiO_2$ | 1623 | 50 | 1 | 3.19 | 2.39 | 4.26 | 1.18 |
| 5 | 〃 | 〃 | $Al_2O_3$ | 1603 | 75 | 1 | 3.22 | 2.41 | 4.30 | 1.20 |
| 6 | 〃 | 〃 | $Si_3N_4$ | 1623 | 100 | 1 | 3.18 | 2.43 | 4.16 | 1.16 |
| 7 | 〃 | 〃 | BN | 1623 | 50 | 2 | 3.21 | 2.48 | 4.15 | 1.15 |
| 8 | 〃 | 〃 | $B_4C$ | 1623 | 50 | 1 | 3.20 | 2.51 | 4.08 | 1.13 |
| 9 | 〃 | 〃 | TiN | 1603 | 50 | 1 | 3.16 | 2.47 | 4.04 | 1.12 |
| 10 | 〃 | 〃 | $Fe_3O_4$ | 1573 | 50 | 1 | 3.25 | 2.38 | 4.44 | 1.23 |
| 比較例1 | 〃 | 〃 | なし | 1573 | 50 | 1 | 3.00 | 2.50 | 3.60 | 1.00 |
| 比較例2 | 〃 | 〃 | なし | Ptペーストで接合 | | | 2.75 | 3.25 | 2.33 | 0.65 |

【0064】

【表2】

| No. | 電極 高温側 | 電極 低温側 | 絶縁材料 | 接合条件 温度(K) | 接合条件 圧力(Mpa) | 接合条件 時間(sec) | 起電力 (V) | 抵抗 (Ω) | 出力電力 (W) | 電力比率 |
|---|---|---|---|---|---|---|---|---|---|---|
| 11 | Pt | Pt | $Fe_3O_4$ | 1573 | 50 | 600 | 3.31 | 2.32 | 4.72 | 1.18 |
| 12 | Pt | Cu | $Fe_3O_4$ | 1323 | 50 | 600 | 3.46 | 2.29 | 5.23 | 1.31 |
| 13 | Pt | Ag | $Fe_3O_4$ | 1223 | 50 | 600 | 3.16 | 2.37 | 4.21 | 1.05 |
| 14 | Pt | Ti | $Fe_3O_4$ | 1373 | 50 | 600 | 3.04 | 2.42 | 3.82 | 0.95 |
| 15 | Pt | Au | $Fe_3O_4$ | 1323 | 50 | 600 | 3.51 | 2.28 | 5.40 | 1.35 |
| 16 | Pt | Au | $Al_2O_3$ | 1323 | 50 | 600 | 3.49 | 2.30 | 5.30 | 1.32 |
| 17 | Pt | Au | $SiO_2$ | 1323 | 50 | 600 | 3.46 | 2.32 | 5.16 | 1.29 |
| 18 | Pt | Au | $Si_{0.95}Ge_{0.05}$ | 1323 | 50 | 600 | 3.48 | 2.27 | 5.33 | 1.33 |
| 19 | Pt | Au | $Si_3N_4$ | 1323 | 50 | 600 | 3.22 | 2.33 | 4.45 | 1.11 |
| 20 | Pt | Au | TiN | 1323 | 50 | 600 | 3.26 | 2.35 | 4.52 | 1.13 |
| 比較例3 | なし | なし | $Fe_3O_4$ | 1573 | 50 | 600 | 3.25 | 2.38 | 4.44 | 1.11 |
| 比較例4 | Pt | Au | なし | 1573 | 50 | 600 | 3.15 | 2.48 | 4.00 | 1.00 |
| 比較例5 | Pt | Pt | なし | Ptペーストで接合 | | | 2.75 | 3.25 | 2.33 | 0.58 |

【0065】

＊ ＊【表3】

| No. | 電極ペースト | | 絶縁ペースト | 焼成条件 | 起電力 | 抵抗 | 出力電力 | 電力比率 |
|---|---|---|---|---|---|---|---|---|
| | 高温側 | 低温側 | | 温度(K) | (V) | (Ω) | (W) | |
| 21 | Pt | Pt | $Fe_3O_4$ | 1273 | 3.06 | 2.30 | 4.07 | 1.02 |
| 22 | Pt | Cu | $Fe_3O_4$ | 1223 | 3.17 | 2.26 | 4.45 | 1.11 |
| 23 | Pt | Ag | $Fe_3O_4$ | 1173 | 3.08 | 2.35 | 4.04 | 1.01 |
| 24 | Pt | Ti | $Fe_3O_4$ | 1223 | 2.98 | 2.40 | 3.70 | 0.92 |
| 25 | Pt | Au | $Fe_3O_4$ | 1223 | 3.32 | 2.25 | 4.90 | 1.22 |
| 26 | Pt | Au | $Al_2O_3$ | 1223 | 3.27 | 2.29 | 4.67 | 1.17 |
| 27 | Pt | Au | $SiO_2$ | 1223 | 3.28 | 2.31 | 4.66 | 1.16 |
| 28 | Pt | Au | $Si_{0.95}Ge_{0.05}$ | 1223 | 3.30 | 2.24 | 4.86 | 1.22 |
| 29 | Pt | Au | $Si_3N_4$ | 1223 | 3.22 | 2.31 | 4.49 | 1.12 |
| 30 | Pt | Au | TiN | 1223 | 3.27 | 2.33 | 4.59 | 1.15 |
| 比較例6* | なし | なし | $Fe_3O_4$ | − | 3.25 | 2.38 | 4.44 | 1.11 |
| 比較例7* | Pt | Au | なし | − | 3.15 | 2.48 | 4.00 | 1.00 |

*P/N一体化焼結材

【0066】
【発明の効果】この発明による熱電変換素子は、Si系やセラミックスの粉末など絶縁材を、pn接合予定部以外に介在させて粉末冶金法などにて一体化することにより、一体化が極めて容易になると共に、pn接合部のロスは大幅に低下し、熱電変換効率が向上し、特に安価で軽量なSi基材料の熱電変換効率を著しく高め、熱応力により接合部が剥がれたり割れたりすることのない構成となすことができる。

【0067】また、この発明によると、熱電変換素子に温度勾配を与えた際の高温側と低温側に位置するpn接合部に異種金属を介して接合し、素子化することにより、起電力および電力量が向上する。

【図面の簡単な説明】

【図1】AとBはこの発明による熱電変換素子の製造方法を示す材料の配置説明図であり、それぞれ粉末冶金法にて直接pn接合する場合である。

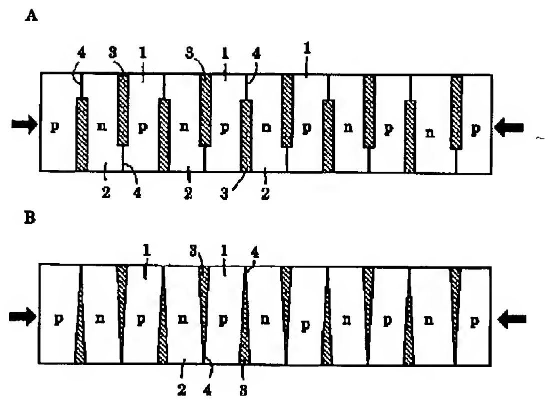
【図2】Aはこの発明による熱電変換素子の製造方法を示す材料の配置説明図であり、電極粉末を介在させて粉末冶金法にてpn接合する場合であり、Bは成形体を示し、CはAにおける絶縁材料粉末と電極粉末の配置形状が異なる場合を示す。

【図3】Aはこの発明による熱電変換素子の製造方法を示す材料の配置説明図であり、薄板電極を介在させて粉末冶金法にてpn接合する場合であり、Bはバルク材料同士をを圧着法にてpn接合する場合、Cはバルク材料にペーストを用いた場合を示す。

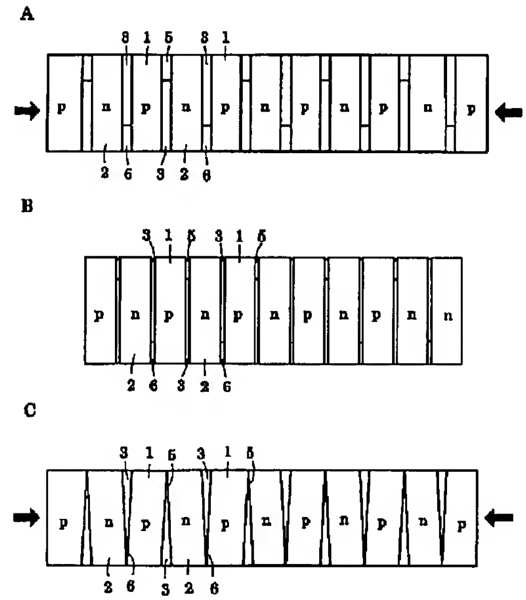
【符号の説明】

1 p型半導体材料粉末
2 n型半導体材料粉末
3 絶縁材料粉末
4 pn接合予定部
5 電極材料粉末(低温側)
6 電極材料粉末(高温側)
7 電極材料(低温側)
8 電極材料(高温側)
10 p型半導体材料
11 n型半導体材料
12 絶縁材料
13 電極材料(低温側)
14 電極材料(高温側)
15 ペースト状絶縁材料
16 ペースト状電極材料(低温側)
17 ペースト状電極材料(高温側)

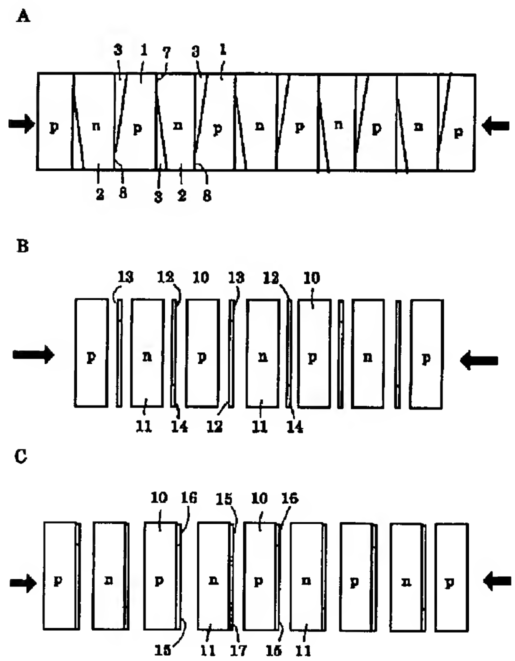
【図1】



【図2】



【図3】



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CLAIMS

[Claim(s)]
[Claim 1] The thermoelectric element which intervenes an insulating material, is unified between a n-type-semiconductor ingredient and a p type semiconductor ingredient, and has an unit or two or more pn junction sections in the connection direction.
[Claim 2] The thermoelectric element which intervenes an electrode material and an insulating material, is unified between a n-type-semiconductor ingredient and a p type semiconductor ingredient, and has an unit or two or more pn junction sections in the connection direction.
[Claim 3] The thermoelectric element according to claim 1 or 2 whose unification is what is depended on powder-metallurgy processing, the sticking-by pressure method, the calcinating method, or welding.
[Claim 4] The thermoelectric element according to claim 3 which is an ingredient which is different by the elevated-temperature [ at the time of the ability of an electrode material to give a temperature gradient ], and low temperature side.
[Claim 5] The manufacture approach of the thermoelectric element which forms an unit or two or more pn junction sections for a n-type-semiconductor powder ingredient and a p type semiconductor powder ingredient the insulating material of tabular or powder, or in the thermoelectric element of one apparatus which has arranged through the electrode material of tabular or powder further, unified with powder-metallurgy processing, and was obtained.
[Claim 6] The manufacture approach of the thermoelectric element which forms an unit or two or more pn junction sections for the n-type-semiconductor ingredient and p type semiconductor ingredient of bulk the insulating material of the shape of tabular or a paste, or in the thermoelectric element of one apparatus which has arranged through the electrode material of the shape of tabular or a paste further, unified by the sticking-by pressure method, and was obtained.
[Claim 7] The manufacture approach of the thermoelectric element which forms an unit or two or more pn junction sections for the n-type-semiconductor ingredient and p type semiconductor ingredient of bulk a paste-like insulating material or in the thermoelectric element of one apparatus which has arranged through a paste-like electrode material further, unified by the calcinating method, and was obtained.
[Claim 8] The manufacture approach of a thermoelectric element given in either of claim 5 to claims 7 which arrange an electrode material which is different, respectively in an elevated-temperature [ at the time of giving a temperature gradient as a component ], and low temperature side.

[Translation done.]

## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] the manufacture whose invention of this used the thermoelectrical conversion ingredient of Si radical etc. -- an easy thermoelectric element is started, arrange n mold and a p type semiconductor in by turns, an electrode material and an insulating material are made to be placed between each, pn junction is carried out with unification shaping, and it is related with the thermoelectric element which the thermoelectrical conversion efficiency of the charge of Si base material is raised remarkably, and can take out electrical energy efficient, and its manufacture approach.
[0002]
[Description of the Prior Art] A thermoelectric element is a device with which the spotlight is captured from the point of energy including CO2 reduction in recent years, and an environmental problem, and utilization is especially expected from a viewpoint of a deployment of heat energy.
[0003] For example, a very wide range application, such as using the waste heat of concomitant use with the pocket power plant for obtaining the electrical and electric equipment simply, the flame sensor of a gas appliance, a solar battery, or a fuel cell and the internal combustion engine of an automobile, and carrying out improvement in fuel consumption in the system, the outdoors, and space which are changed into electrical energy using waste heat, such as an incinerator and a turbine of an electric power plant, is examined.
[0004] However, the thermoelectric element known until now has come to be used widely from the reasons nil why the raw material and manufacturing cost which generally have the problem of the environmental pollution of a use element that conversion efficiency is low and that operating temperature limits are very narrow are high etc.
[0005] The conversion efficiency of this heat energy to electric ENERUGIHE is the function of a performance index ZT, and becomes so high that ZT is high. This performance index ZT is ZT=S2sigma T/kappa. It is expressed like a formula. Here, S is the absolute temperature which conductivity and kappa expressed the Seebeck coefficient of thermoelectric material, and sigma, and expressed thermal conductivity and T with the average of (TL) the (TH) and low temperature side the elevated-temperature side of a thermoelement.
[0006] The thermoelectric material of current and the highest performance index is IrSb3 (T. Calllet, A.Borshchrysky and J.-P.Fleurial:Proc.12th Int.Conf.on Thermoelectrics, P(Yokohama, Japan, 1993) 132.) which has the SUKUTTERUDAITO mold crystal structure, and the ZT value shows about 2.0. However, since the raw material cost of Ir is high, it has not resulted in utilization.
[0007] Moreover, although Bi2Te3 which shows a high performance index at low temperature was used as components for cooling, such as a semi-conductor, as a Peltier device, since the melting point was as low as 530K, there was a problem that operating temperature limits were narrow.
[0008] On the other hand, although [ point / of cost and an environment ] a Fe-Si system ingredient is promising, the performance index (ZT) was 0.2 or less, and this system was that with which the property demanded as a thermoelectrical conversion ingredient is not filled until.
[0009] The Si-germanium system ingredient reported that thermal conductivity could fall greatly, when B.Abeles (Phys.Rev.131 and 1906 (1963)) investigated the presentation dependency of the thermal conductivity of a Si-germanium alloy and alloyed Si and germanium. By their report, if the content of germanium did not do 20-30 atom % content of, it was reported that the fall of heat conduction was not seen.
[0010] however, that the raw material cost of germanium is high and the condition of the liquidus line and the solidus line of all ****** that Si and germanium are broad -- having -- the dissolution and Zone Leveling -- in law, producing a presentation to homogeneity calls it difficulty -- it was problematic. Moreover, although the approach by the hotpress was also tried in order to make a presentation into homogeneity, it was lacking in mass-production nature.

[0011] Furthermore, the approach of producing the preforming object of disc-like n mold and p mold, carrying out the laminating of the four-sheet preforming object, sintering it in the order of n, p, n, and p, using Si-germanium alloy powder, processing this into a rectangular parallelepiped after that, performing cutting which forms the separation section between n and p further to JP,11-54808,A, and producing a thermoelectric element with a configuration which is fold up is propose. However, it not only requires time and effort, but a production process is complicated and the property of the ingredient itself is inferior to processing in it.

[0012]

[Problem(s) to be Solved by the Invention] Artificers did the knowledge of the ability to become the thermoelectrical conversion ingredient which has a high performance index by addition of the little element 0.001 to 20 atom % to Si, as a result of Si currently widely used as a semiconductor device evaluating the thermoelectrical property of the ingredient of Si radical especially paying attention to having a very high Seebeck coefficient (WO 99/22410).

[0013] An environmental load is also small, Si is in abundance and a resource also has the description of being light, the top where raw material cost is also comparatively cheap. Furthermore, artificers found out improving as power which can enlarge a Seebeck coefficient and can take it out by selecting the electrode of a joint.

[0014] However, in case a thermoelectrical conversion ingredient is used as a component, when the junction about the joint and electrode of an ingredient of p mold and n mold is not good, a loss arises to the power which can be taken out. This may happen, even when the electrode quality of the material is selected. Furthermore, junction of the electrode of an elevated-temperature edge was alloyed depending on diffusion of thermoelectric material and the atom of the electrode quality of the material, or the case, and when the difference of the coefficient of thermal expansion between the electrode quality of the materials was large, there was a problem constituting peeling of an electrode or the cause of a crack.

[0015] This invention aims at offer of the thermoelectric element using the thermoelectrical conversion ingredient of Si radical with which manufacture consists of an easy configuration, and its manufacture approach while it is the configuration which raised remarkably the thermoelectrical conversion efficiency of a thermoelectrical conversion ingredient and the especially cheap and lightweight charge of Si base material.

[0016]

[Means for Solving the Problem] Artificers as an approach of taking out power as a thermoelectric element, without spoiling thermoelectrical properties, such as Si radical thermoelectrical conversion ingredient It notes unifying and producing the ingredient of n mold and p mold. As the unification approach It tried by the approach carry out patterning of the resist of a powder ingredient, and it carries out a laminating on Si substrate besides the powder metallurgy means of sintering powder after compression molding between heat, such as a hotpress, discharge plasma sintering, and a hot isostatic press, or cold compression molding.

[0017] While unification becomes very easy on the occasion of unification by making insulating materials, such as Si system and powder of the ceramics, intervene in addition to the pn junction schedule section, artificers That the loss of the pn junction section falls sharply and thermoelectrical conversion efficiency improves, and by producing the sintered compact which has arranged the ingredient by turns further and was united with p/n/p/n/p/ The knowledge of the ability of most losses by electrode junction to produce the component which becomes so small that it can ignore, and a joint separates with thermal stress or does not break was carried out.

[0018] Moreover, artificers are joined to the pn junction section located in an elevated-temperature [ at the time of giving a temperature gradient to a thermoelectric element ], and low temperature side through a dissimilar metal. How to try to component-ize and insert metal powder in the interface of the powder of p/n as the junction approach at the time of powder sintering, It carried out by the approach of p/n minding a metal plate, and joined with said powder metallurgy means, and as a result of measuring the electrical potential difference and current of a component which were unified, by choosing the metal quality of the material the optimal, the knowledge of electromotive force and electric energy improving was carried out, and this invention was completed.

[0019] Furthermore, it is possible the method of calcinating the bulk and the electrode material of the sintering material of not only the junction by powder metallurgy but the charge of Si base material and ingot material using the sticking-by pressure methods, such as resistance heating, energization sintering, and pressurization between heat, and a paste ingredient and to join with welding process etc. further, and the knowledge of there being no loss of electrode junction and electromotive force and its electric energy improving was carried out by choosing the optimal electrode quality of the material.

[0020] This invention is a thermoelectric element characterized by having the unit or two or more pn junction sections which made the insulating material intervene, or the electrode material and the insulating material were made to intervene, and were unified between the n-type-semiconductor ingredient and the p type semiconductor ingredient.

[0021] This invention a n-type-semiconductor powder ingredient and a p type semiconductor powder ingredient

moreover, [ the insulating material of tabular or powder, or ] [ whether it unifies with powder-metallurgy processing by arranging through an electrode material further, and ] Or a solid n-type-semiconductor ingredient and a solid p type semiconductor ingredient are arranged through an electrode material to the insulating material or pan of the shape of tabular, powder, or a paste. It is the manufacture approach of the thermoelectric element characterized by unifying by the sticking-by pressure method or the calcinating method between the colds or between heat, and forming an unit or two or more pn junction sections in the thermoelectric element of obtained one apparatus.
[0022] Furthermore, this invention is the thermoelectric element characterized by arranging an electrode material which is different, respectively in an elevated-temperature [ at the time of giving a temperature gradient as a component ], and low temperature side, and its manufacture approach.
[0023]
[Embodiment of the Invention] The manufacture approach of the thermoelectric element by this invention is explained in full detail based on a drawing. Drawing 1 A is the case where direct pn junction is carried out with powder-metallurgy processing, and the ingredient powder which can be sintered, respectively as the p type semiconductor ingredient powder 1, the n-type-semiconductor ingredient powder 2, and insulating material powder 3 is used for it.
[0024] For example, into box-like metal mold, the diaphragm of a tuning fork mold is used so that an aperture side may interchange by turns, the p type semiconductor ingredient powder 1, the n-type-semiconductor ingredient powder 2, and the insulating material powder 3 are inserted by turns, a diaphragm is removed, a lid is formed in a top face, and it compresses in the direction of an arrow head to a metal mold core, and makes with a Plastic solid.
[0025] A Plastic solid consists of a configuration which the p type semiconductor ingredient powder 1 and the n-type-semiconductor ingredient powder 2 were separated with the insulating material powder 3 except for the pn junction schedule section 4, and was arranged by turns. Here, by sintering this Plastic solid, between each semiconductor material, an insulating material is unified and the thermoelectric element of one apparatus which has two or more pn junction sections directly joined by sintering in the connection direction of each semiconductor material is obtained.
[0026] Moreover, in drawing 1 A, even if it changes into an insulating material plate, an insulating material sheet, etc. which fabricated insulating material powder 3 part beforehand, of course, as for the ability of the direct pn junction section by sintering to manufacture the thermoelectric element of two or more connection molds, the direct pn junction section can manufacture the thermoelectric element of one 1 pair mold similarly.
[0027] The example of manufacture shown in drawing 1 B inserts the p type semiconductor ingredient powder 1, the n-type-semiconductor ingredient powder 2, and the insulating material powder 3 by turns, as a triangular diaphragm is used into box-like metal mold so that an aperture side may interchange by turns, and insulating material powder does not go into the necessary point of a triangular diaphragm, it removes a diaphragm, compresses it in the direction of an arrow head to a metal mold core, and is made with a Plastic solid.
[0028] A Plastic solid serves as a configuration which the p type semiconductor ingredient powder 1 and the n-type-semiconductor ingredient powder 2 were separated with the insulating material powder 3 except for the pn junction schedule section 4, and was arranged by turns. By sintering this Plastic solid, between each semiconductor material, an insulating material is unified and the thermoelectric element of one apparatus which has two or more pn junction sections directly joined by sintering in the connection direction of each semiconductor material is obtained.
[0029] In box-like metal mold, like illustration, the example of manufacture shown in drawing 2 A loads with the insulating material powder 3 and the electrode material powder 5 and 6 between the p type semiconductor ingredient powder 1 and the n-type-semiconductor ingredient powder 2, and as it loads so that the insertion point of the insulating material powder 3 and the electrode material powder 5 and 6 may put in by turns and may change, and it compresses in the direction of an arrow head to a metal mold core and it is shown at drawing 2 B, it makes them with a Plastic solid.
[0030] Moreover, the elevated-temperature side which made the lower part of the thermoelectric element completed by a diagram approach a heat source, when the temperature gradient which made the upper part the low temperature side is given, the metal of the quality of the material which is different by elevated-temperature side 6 and low temperature side 5, respectively, and alloy powder are used for electrode material powder.
[0031] By sintering this Plastic solid, between each semiconductor material, an insulating material is unified and the thermoelectric element of one apparatus which has two or more pn junction sections joined through the electrode material by sintering in the connection direction of each semiconductor material is obtained.
[0032] Moreover, the rectangle configuration shown in drawing 2 A is loaded with the insulating material powder 3 and the electrode material powder 5 and 6, and also as shown in drawing 2 C, between the p type semiconductor ingredient powder 1 and the n-type-semiconductor ingredient powder 2, loading in the shape of a triangle is also possible, and the gestalt of arbitration can be adopted according to an amount, an insulating dimension, etc. of an insulating material.
[0033] Although the example of manufacture shown in drawing 3 A is the same as that of the above-mentioned

drawing 1 B The sheet metal-like electrode materials 7 and 8 are arranged in the pn junction schedule section of the triangular top-most-vertices section which does not arrange the insulating material powder of drawing 1 B, and others are the things loaded with the insulating material powder 3. By sintering, after making with a compression-molding object, between each semiconductor material, an insulating material is unified and the thermoelectric element of one apparatus which has two or more pn junction sections joined by sintering through electrode materials 7 and 8 in the connection direction of each semiconductor material is obtained. When the temperature gradient which made the upper part the low temperature side the elevated-temperature side which made the lower part of the thermoelectric element completed by a diagram approach a heat source is given to electrode materials 7 and 8, the metal of the quality of the material which is different by elevated-temperature side 8 and low temperature side 7, respectively, and the alloy are used for the electrode material also here.

[0034] The example of manufacture shown in drawing 3 B between the p type semiconductor ingredients 10, such as sintering material which pressed the ingot material or the letter of a block solidified in the shape of a block, and was sintered from the dissolution alloy, and the n-type-semiconductor ingredient 11 By arranging the insulating material 12 and electrode materials 13 and 14 which were processed into the plate, making these contact, and unifying with the sticking-by-pressure means between heat or between the colds Between each semiconductor material, an insulating material is unified and the thermoelectric element of one apparatus by which two or more pn junction sections joined through the electrode material in the connection direction have been arranged is obtained.

[0035] The example of manufacture shown in drawing 3 C applies the paste-like insulating material 15 and the paste-like electrode materials 16 and 17 to one side of the p type semiconductor ingredients 10, such as the aforementioned ingot material or sintering material, and the n-type-semiconductor ingredient 11. By making these contact and unifying by baking, between each semiconductor material, an insulating material is unified and the thermoelectric element of one apparatus by which two or more pn junction sections joined through the electrode material in the connection direction have been arranged is obtained.

[0036] When the temperature gradient which made the upper part the low temperature side the elevated-temperature side which made the lower part of the thermoelectric element completed by a diagram approach a heat source is given to electrode materials 16 and 17, the metal of the quality of the material which is different by elevated-temperature side 17 and low temperature side 16, respectively, and the alloy are used for the electrode material also here. Moreover, it is also possible to change into the insulating material 15 of the shape of an above paste and electrode materials 16 and 17, and to unify with means, such as energization sintering, using the insulating material powder for sintering and electrode material powder.

[0037] As shown in drawing 1 besides the even number mold which begins from p mold and finishes with n mold as an approach of arranging the semiconductor material to unify, odd number molds, such as p, n, p, and n, p, n, p, n, may be used, and it is necessary to consider as the configuration which has the one or more pn junction sections in an articulated section anyway.

[0038] Powder-metallurgy processing, the sticking-by pressure method, the calcinating method, welding process, etc. are employable as the unification shaping approach. powder-metallurgy processing -- for example, the n-type-semiconductor powder ingredient of Si-germanium and a p type semiconductor powder ingredient list -- the plate or powder of a metallic material -- for example, the thermoelectric element of drawing 1 and abbreviation -- it can put into the metal mold of an analog etc. at individual or coincidence, and can unify with the powder metallurgy means of sintering powder after compression molding between heat, such as a hotpress, discharge plasma sintering, and a hot isostatic press, or cold compression molding.

[0039] Moreover, it is still more possible the method of calcinating the charge of Si base material, the sintering material of a Si-germanium alloy, ingot material, and an electrode material using the sticking-by pressure methods, such as resistance heating, energization sintering, and pressurization between heat, and a paste ingredient and to carry out pn junction with welding process etc. The above-mentioned unification shaping approach is good to choose the optimal approach according to the class and gestalt of a semiconductor material, a material for electrode, and an insulating material.

[0040] Furthermore, how patterning of the resist of a powder ingredient is carried out, and it carries out a laminating on Si substrate besides above-mentioned powder-metallurgy processing and an Si1-xGex ($x< 0.20$) substrate is employable. There are specifically PVD which electron beam heating of Si and the germanium is carried out [ PVD ], and evaporates them, a CVD method to which the laminating of Si and the germanium is carried out from SiH4 and GeH4, and junction of a metal layer is also possible in a pn junction list through a mask. Behind a laminating, by heat-treating at 400-800 degrees C, a cascade screen crystallizes and a property improves.

[0041] As an insulating material, any well-known ingredient which can be insulated electric is employable. 102 or more ohm-m of resistivity is desirable. A semiconductor material, sintering, sticking by pressure, and adhesion are

possible, and the ingredient which the coefficient of thermal expansion approximates is desirable. Moreover, since the temperature gradient of a thermoelectrical conversion ingredient will become small if heat conducts from an insulating material, an ingredient with small thermal conductivity is desirable. For example, when semiconductor materials are a charge of Si base material, and a Si-germanium alloy, Si, non doping Si-germanium, SiO2, Si3N4, BN and SiC, aluminum2O3, TiN, various ferrites, etc. can be used.

[0042] The metal and alloy which can use any quality of the materials, such as a metal and resin, are comparatively excellent in corrosion resistance as an electrode material, and are moreover easy to attach in a thermoelectrical conversion ingredient are desirable. It is desirable to use a high-melting metal and an alloy in the thermoelectric material in which a high property is shown especially at an elevated temperature. For example, as an ingredient by the side of the elevated temperature of a thermoelectrical conversion ingredient, Bi, Sn, Ag, Cu, Pt, aluminum, Au, Fe, Mo, Zn, and Pb are desirable as an ingredient by the side of Zr, Au, Ag, Pt, Cu, Ti, Mo, Zn, W, C, and low temperature. Moreover, the alloy of these metals or the alloy containing these metals can also be used.

[0043] The class of metallic material used for an elevated-temperature [ of a thermoelectrical conversion ingredient ] and low temperature side and combination change with thermoelectrical conversion ingredient kinds, respectively. In aluminum and Si1-xGex (x< 0.20), it is [ an elevated-temperature side / a Pt and low temperature side / an elevated-temperature side ] for example, desirable [ aluminum etc. ], when it is Cu and Bi2Te3 compound in a Pt and low temperature side at an elevated-temperature side in the case of FeSi2 compound to a Pt and low temperature side.

[0044] In this invention, any well-known quality of the material is employable as a thermoelectrical conversion ingredient. A Bi2Te3 system [ besides the charge of Si base material and the thermoelectrical conversion ingredient which consists of a presentation of Si1-xGex (x< 0.20) ] ingredient is especially desirable.

[0045] The presentation of the charge of Si base material is Si1-xAx (x< 0.20). To A 4 group element (germanium, C, Sn), It is what adds at least one sort of a 3-5 group compound semiconductor and a 2-6 group compound semiconductor, and controls carrier concentration by the dopant element mentioned later to 1017-1021 (M/m3). Most of the inside of each crystal grain is Si in Polycrystal Si fundamentally, and, in said alloying element and dopant element, and Si-germanium, it is characterized by the structure which germanium and a dopant element segregated at coincidence at the grain boundary section.

[0046] A Seebeck coefficient is very large by adjusting compound addition and its addition, thermoelectrical conversion efficiency can be raised remarkably, and the charge of Si base material is that various alloying elements, such as P, B, and aluminum, are independent or a cheap thermoelectrical conversion ingredient by which productivity is good and quality was stabilized so that the carrier concentration in Si semi-conductor may be set to 1017-1021 (M/m3).

[0047] It becomes the cause of a Seebeck coefficient high [ of Si ] falling since germanium is spread also in Si rich phase in a grain at coincidence and it dissolves, although, especially as for a high performance index, germanium is not obtained in the charge of Si base material of this invention in Si-germanium since thermal conductivity is large at under 0.05 atom %, and thermal conductivity falls a little above 20 atom %, and reducing a performance index. Therefore, let the desirable content of germanium be the range of 0.05 or more and under 20 atom %. It is three to 10 atom % especially preferably.

[0048] In this invention, the dopant element for making Si with a P-type semiconductor or an N-type semiconductor is added in order to obtain a high Seebeck coefficient, at the same time it reduces the heat conductivity and electric resistance by the carrier concentration of necessary within the limits. If the application of a thermoelectrical conversion ingredient is taken into consideration, since it will change according to applications, such as size of a heat source, a use part and a gestalt, the current to treat, and an electrical potential difference, by whether emphasis is put on which property of a Seebeck coefficient, conductivity, and thermal conductivity, a selection element and its addition can be chosen according to an application etc. As an addition, 0.001 atoms % - 20 atom % is desirable.

[0049] As a dopant element for making with a p type semiconductor, one sort chosen from each group of p group group (Be, Mg, calcium, Sr, Ba, Zn, Cd, Hg, B, aluminum, Ga, In, Tl) and transition-metals element M1 group (M1;Y, Mo, Zr) or two sorts or more are desirable. Especially desirable elements are B, Ga, and aluminum especially.

[0050] The dopant element for making with a n-type semiconductor n group group (N, P, As, Sb, Bi, O, S, Se, Te), transition-metals element M2 group (it Os(es), Ir(s), Pt(s) and Au(s) M2;Ti, and V, Cr, Mn, Fe, Co, nickel, Cu, Nb, Ru, Rh, Pd, Ag, Hf, Ta, W and Re --) However, one sort chosen from each group of the rare-earth-elements group RE (RE;La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu) or two sorts or more of Fe are desirable below 10 atom %. Especially desirable elements are P, Cu, and As especially.

[0051]

[Example] As example 1 raw material, Si0.95germanium0.05 (B0.3at%) was blended with p mold, Si0.95germanium0.05 (P0.4at%) was blended with n mold, and the jet mill ground the ingot of the thermoelectrical

conversion ingredient of p mold which dissolved with the RF vacuum melting furnace, and n mold in mean particle diameter of about 4 micrometers in a vibration mill and nitrogen gas.

[0052] The pn junction section which loaded with so that it might become the configuration of the p type semiconductor ingredient powder 1 and the n-type-semiconductor ingredient powder 2 having been separated by the carbon mold with the insulating material powder 3 except for the pn junction schedule section 4, and having arranged each obtained powder by turns in it like drawing 1 A, and was unified with the hotpress on condition that 1500-1600Kx1h and pressure 25-100MPa produced the thermoelectric element which has ten places.

[0053] The dimension of the whole component was 5mmx75mmx15mm. The amount of output power of the component which joined lead wire to the electrode to both ends most, heated one side to the elevated temperature of 873K, gave the temperature gradient of 373K for another side, measured each generating electromotive force, a generating electromotive style, and resistance by the multimeter, and was obtained was calculated. The result is shown in Table 1. In addition, the rate of a power ratio measured the output power of the following examples 1 (with no insulating material) of a comparison as 1.

[0054] The measured value (example 2 of a comparison) at the time of joining as an example of a comparison through the measured value (example 1 of a comparison) and Pt paste when not inserting an insulating material is similarly shown in Table 1.

[0055] As example 2 raw material, Si0.95germanium0.05 (B0.3at%) was blended with p mold, Si0.95germanium0.05 (P0.4at%) was blended with n mold, and the stamp mill and the ball mill ground the ingot of the thermoelectrical conversion ingredient of p mold which dissolved by the arc dissolution, and n mold in mean particle diameter of about 2 micrometers. The ball mill was performed in the xylene solvent.

[0056] It loaded with each obtained powder so that it might load with the insulating material powder 3 and the electrode material powder 5 and 6 with a particle size of 10 micrometers between the p type semiconductor ingredient powder 1 and the n-type-semiconductor ingredient powder 2, the insertion point of the insulating material powder 3 and the electrode material powder 5 and 6 might put in by turns and it might change like drawing 2 A, and it carried out discharge plasma sintering on condition that 1100 - 1573Kx600sec and pressure 50MPa, and the thermoelectric element with the ten pn junction sections was produced.

[0057] The dimension of the whole component was 5mmx75mmx15mm. Lead wire was joined to the electrode to the No. 1 both ends of the component, one side was heated to the elevated temperature of 873K, the temperature gradient of 373K was given for another side, each generating electromotive force, a generating electromotive style, and resistance were measured by the multimeter, and the obtained amount of output power was calculated. The result is shown in Table 2. In addition, the rate of a power ratio measured the output power of the following examples 4 (with no insulating material) of a comparison as 1.

[0058] In addition, although an insulating material is inserted into the measured value (example 5 of a comparison) at the time of joining as an example of a comparison through the measured value (example 4 of a comparison) and Pt paste when not inserting an insulating material, and the pn junction section, the measured value (example 3 of a comparison) of the component which does not mind a metal plate is similarly shown in Table 2.

[0059] As example 3 raw material, Si0.95germanium0.05 (B0.3at%) was blended with p mold, Si0.95germanium0.05 (P0.4at%) was blended with n mold, and the jet mill ground the ingot of the thermoelectrical conversion ingredient of p mold which dissolved with the RF vacuum melting furnace, and n mold in mean particle diameter of about 4 micrometers in a vibration mill and nitrogen gas. Each obtained powder was inserted in the 5mmx5mmx15mm carbon mold, and the hotpress was carried out by 1573Kx1h and pressure 50MPa.

[0060] As it was obtained and was shown in ******** at drawing 3 C, the paste-like insulating material 15 and the low-temperature lateral electrode paste 16 were applied to the ingredient of p mold, and the paste-like insulating material 15 and the elevated-temperature lateral electrode paste 17 were applied to the ingredient of n mold, and it calcinated in 1173Kx30min and a vacuum after that, and the thermoelectric element with the ten pn junction sections was produced.

[0061] The amount of output power of a thermoelectric element which joined lead wire to the electrode to both ends most, heated one side to the elevated temperature of 873K, gave the temperature gradient of 373K for another side, measured each generating electromotive force, a generating electromotive style, and resistance by the multimeter, and was obtained was calculated. The result is shown in Table 3. In addition, the rate of a power ratio measured the output power of the following examples 7 (with no insulating paste) of a comparison as 1.

[0062] In addition, although an insulating paste is inserted into the measured value (example 7 of a comparison) and the pn junction section when not inserting an insulating paste as an example of a comparison, the measured value (example 6 of a comparison) of the component which does not mind electrode paste is similarly described in Table 3.

[0063]

[Table 1]

| No. | N型材料 | P型材料 | 絶縁材料 | 焼結条件 温度(K) | 焼結条件 圧力(Mpa) | 焼結条件 時間(h) | 起電力 (V) | 抵抗 (Ω) | 出力電力 (W) | 電力比率 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $Si_{0.95}Ge_{0.05}$ (P 0.4at%) | $Si_{0.95}Ge_{0.05}$ (B 0.3at%) | $Si_{0.95}Ge_{0.05}$ | 1523 | 50 | 1 | 3.05 | 2.48 | 3.75 | 1.04 |
| 2 | 〃 | 〃 | $Si_{0.95}Ge_{0.05}$ | 1573 | 50 | 1 | 3.13 | 2.44 | 4.02 | 1.12 |
| 3 | 〃 | 〃 | $SiO_2$ | 1573 | 30 | 1 | 3.12 | 2.46 | 3.96 | 1.10 |
| 4 | 〃 | 〃 | $SiO_2$ | 1623 | 50 | 1 | 3.19 | 2.39 | 4.26 | 1.18 |
| 5 | 〃 | 〃 | $Al_2O_3$ | 1603 | 75 | 1 | 3.22 | 2.41 | 4.30 | 1.20 |
| 6 | 〃 | 〃 | $Si_3N_4$ | 1623 | 100 | 1 | 3.18 | 2.43 | 4.16 | 1.16 |
| 7 | 〃 | 〃 | BN | 1623 | 50 | 2 | 3.21 | 2.48 | 4.15 | 1.15 |
| 8 | 〃 | 〃 | $B_4C$ | 1623 | 50 | 1 | 3.20 | 2.51 | 4.08 | 1.13 |
| 9 | 〃 | 〃 | TiN | 1603 | 50 | 1 | 3.16 | 2.47 | 4.04 | 1.12 |
| 10 | 〃 | 〃 | $Fe_3O_4$ | 1573 | 50 | 1 | 3.25 | 2.38 | 4.44 | 1.23 |
| 比較例1 | 〃 | 〃 | なし | 1573 | 50 | 1 | 3.00 | 2.50 | 3.60 | 1.00 |
| 比較例2 | 〃 | 〃 | なし | Ptペーストで接合 | | | 2.75 | 3.25 | 2.33 | 0.65 |

[0064]
[Table 2]

| No. | 電極 | | 絶縁材料 | 接合条件 | | | 起電力 (V) | 抵抗 (Ω) | 出力電力 (W) | 電力比率 |
|---|---|---|---|---|---|---|---|---|---|---|
| | 高温側 | 低温側 | | 温度(K) | 圧力(Mpa) | 時間(sec) | | | | |
| 11 | Pt | Pt | $Fe_3O_4$ | 1573 | 50 | 600 | 3.31 | 2.32 | 4.72 | 1.18 |
| 12 | Pt | Cu | $Fe_3O_4$ | 1323 | 50 | 600 | 3.46 | 2.29 | 5.23 | 1.31 |
| 13 | Pt | Ag | $Fe_3O_4$ | 1223 | 50 | 600 | 3.16 | 2.37 | 4.21 | 1.05 |
| 14 | Pt | Ti | $Fe_3O_4$ | 1373 | 50 | 600 | 3.04 | 2.42 | 3.82 | 0.95 |
| 15 | Pt | Au | $Fe_3O_4$ | 1323 | 50 | 600 | 3.51 | 2.28 | 5.40 | 1.35 |
| 16 | Pt | Au | $Al_2O_3$ | 1323 | 50 | 600 | 3.49 | 2.30 | 5.30 | 1.32 |
| 17 | Pt | Au | $SiO_2$ | 1323 | 50 | 600 | 3.46 | 2.32 | 5.16 | 1.29 |
| 18 | Pt | Au | $Si_{0.95}Ge_{0.05}$ | 1323 | 50 | 600 | 3.48 | 2.27 | 5.33 | 1.33 |
| 19 | Pt | Au | $Si_3N_4$ | 1323 | 50 | 600 | 3.22 | 2.33 | 4.45 | 1.11 |
| 20 | Pt | Au | TiN | 1323 | 50 | 600 | 3.26 | 2.35 | 4.52 | 1.13 |
| 比較例3 | なし | なし | $Fe_3O_4$ | 1573 | 50 | 600 | 3.25 | 2.38 | 4.44 | 1.11 |
| 比較例4 | Pt | Au | なし | 1573 | 50 | 600 | 3.15 | 2.48 | 4.00 | 1.00 |
| 比較例5 | Pt | Pt | なし | Ptペーストで接合 | | | 2.75 | 3.25 | 2.33 | 0.58 |

[0065]
[Table 3]

| No. | 電極ペースト 高温側 | 電極ペースト 低温側 | 絶縁ペースト | 焼成条件 温度(K) | 起電力 (V) | 抵抗 (Ω) | 出力電力 (W) | 電力比率 |
|---|---|---|---|---|---|---|---|---|
| 21 | Pt | Pt | $Fe_3O_4$ | 1273 | 3.06 | 2.30 | 4.07 | 1.02 |
| 22 | Pt | Cu | $Fe_3O_4$ | 1223 | 3.17 | 2.26 | 4.45 | 1.11 |
| 23 | Pt | Ag | $Fe_3O_4$ | 1173 | 3.08 | 2.35 | 4.04 | 1.01 |
| 24 | Pt | Ti | $Fe_3O_4$ | 1223 | 2.98 | 2.40 | 3.70 | 0.92 |
| 25 | Pt | Au | $Fe_3O_4$ | 1223 | 3.32 | 2.25 | 4.90 | 1.22 |
| 26 | Pt | Au | $Al_2O_3$ | 1223 | 3.27 | 2.29 | 4.67 | 1.17 |
| 27 | Pt | Au | $SiO_2$ | 1223 | 3.28 | 2.31 | 4.66 | 1.16 |
| 28 | Pt | Au | $Si_{0.95}Ge_{0.05}$ | 1223 | 3.30 | 2.24 | 4.86 | 1.22 |
| 29 | Pt | Au | $Si_3N_4$ | 1223 | 3.22 | 2.31 | 4.49 | 1.12 |
| 30 | Pt | Au | TiN | 1223 | 3.27 | 2.33 | 4.59 | 1.15 |
| 比較例6* | なし | なし | $Fe_3O_4$ | － | 3.25 | 2.38 | 4.44 | 1.11 |
| 比較例7* | Pt | Au | なし | － | 3.15 | 2.48 | 4.00 | 1.00 |

*P/N一体化焼結材

[0066]
[Effect of the Invention] While unification becomes very easy by the thermoelectric element by this invention making insulating materials, such as Si system and powder of the ceramics, intervene in addition to the pn junction schedule section, and unifying it with powder-metallurgy processing etc., the loss of the pn junction section falls sharply, its thermoelectrical conversion efficiency improves, and especially, it can raise remarkably the thermoelectrical conversion efficiency of the cheap and lightweight charge of Si base material, and can be made with the configuration of a joint separating with thermal stress or not being divided.
[0067] Moreover, according to this invention, electromotive force and electric energy improve by joining and component-izing through a dissimilar metal in the pn junction section located in an elevated-temperature [ at the time of giving a temperature gradient to a thermoelectric element ], and low temperature side.

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[Translation done.]